Chapter VI

Field Methods For The Analysis Of Petroleum Hydrocarbons

Contents

Exhibits

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Petroleum Hydrocarbons

Analysis of soil, soil-gas, and groundwater samples in the field is an essential element of expedited site assessments (ESAs). Field managers require field-generated data in order to complete a site assessment in a single mobilization. In recent years many field methods for petroleum hydrocarbon analysis have been developed and improved. These technological improvements can change the way site assessments are conducted by providing reliable data in the field that can then be used to select subsequent sampling locations.

Historically, the analysis of contaminated media during UST site assessments has been completed off-site in fixed laboratories that use certified analytical methods. While these methods provide a very high data quality level (DQL), their results may take days or weeks and their cost is relatively high. In addition, many studies have shown that samples can undergo significant degradation during the shipping and holding times before analysis.

The development and improvement of many field methods have allowed site assessments to be performed more rapidly and completely than is feasible with off-site analysis. By combining field methods of different DQLs, ESAs can improve the resolution of contaminant distribution and minimize analytical costs. Low DQL (*i.e.*, screening) methods can be used to provide a high density of data to determine source areas (*i.e.*, zones of non-aqueous-phase liquid [NAPL] contamination). Higher DQL methods can be used to identify low concentrations or specific chemicals of concern at select locations (*e.g.*, leading edge of contaminant plume). Data from higher DQL methods can also be used as part of a quality control check for the field analytical program.

Exhibit VI-1 is a summary table of the primary selection criteria for eight commonly available field methods applicable for the analysis of petroleum hydrocarbons. It is followed by a brief discussion of the DQL system used in this chapter. The majority of the chapter is dedicated to discussions of the eight field methods listed in Exhibit VI-1. Each method is summarized with a capabilities and limitations table. A brief description and discussion of emerging technologies (*i.e.*, new technologies that are subject to significant innovation in the immediate future) appears at the end of the chapter. In addition, Appendix B, at the end of the manual, provides the reader with a table of relevant U.S. EPA test methods for petroleum hydrocarbons.

The chapter is organized so that readers can use the summary table (Exhibit VI-1) for initial selection of the most appropriate methods for a specific situation. They can then make a final selection by referring to the discussions of the individual methods that follow. The simpler, lower DQL methods are presented first.

Exhibit VI-1
Summary Table Of Field Methods For Petroleum Hydrocarbon Analysis

Test Method	Media[1]			Analyte	Data Quality Level[2]	Analysis Time	Cost Per Sample[3]	Skill Level	Limitations
	S	SG	W						
Detector Tubes		✓	✓	>100 specific compounds	1A/1B	5 to 15 min	$8 to $27	Low	High degree of cross-reactivity
Fiber Optic Chemical Sensors		✓	✓	VOCs and SVOCs $\geq C_6$	1A/1B	3 to 5 min	<$1 to $10	Low	Does not measure specific constituents
Colorimetric Test Kits	✓		✓	Aromatic hydrocarbons	1A/1B	10 to 20 min	$17 to $42	Low-Medium	Colors may be difficult to distinguish
TOV Methods With FID/PID	✓	✓	✓	Total VOCs	1A/1B	1 to 30 min	<$1 to $10	Low-Medium	Does not measure specific constituents
Turbidimetric Test Kit	✓			TPH of mid-range hydrocarbons (*e.g.*, diesel fuel)	1B	15 to 20 min (25 per hour)[4]	$10 to $15	Low-Medium	Not useful for gasoline
Immunoassay Test kits	✓		✓	TEX/PAHs/ TPH	1B	30 to 45 min (5 to 8 per hour)[4]	$20 to $60	Medium	Cross-reactivity may affect interpretation
Portable Infrared Detectors	✓		✓	TPH of hydrocarbons C_6 to C_{26}	2	5 to 20 min	$5 to $30	Medium	VOCs are not accurately analyzed
Field GC	✓	✓	✓	Specific VOCs and SVOCs	2/3	10 to 60 min[5]	$20 to $70	Medium-High	Requires a skilled technician

[1] Soil (S), Soil-Gas (SG), Water (W)
[2] Data quality levels are discussed in further detail in the following text
[3] Includes estimation of capital costs and disposables -- excludes labor
[4] When run in batches
[5] Longer times result when high quality method preparations are performed

Data Quality Levels

Data quality levels (DQLs) represent a classification system of analytical methods by the quality of data they provide. DQLs are one of several criteria that can be used for selecting an appropriate analytical method. Exhibit VI-2 presents the summary table of the DQL classification system used in this manual, which was adapted from the classification system developed by the New Jersey Department of Environmental Protection (1994).   The levels are organized in a data quality hierarchy in which DQL 1 provides screening information, DQL 2 provides quantitative data, and DQL 3 provides the most rigorous quantitative data. Every state will have its own definition and requirements for various field analytical methods and its own DQLs, so a complete list of QA/QC procedures for each level is not provided.

Data Quality Level 1: Screening

DQL 1 screening methods are divided into two subgroups: 1A and 1B. Both are used for an initial screening of samples or for health and safety evaluations. DQL 1A provides a general indication of the presence of contaminants, DQL 1B provides relative numerical values. All DQL 1 methods:

- May require confirmation with higher DQL methods; and
- Detect the presence of classes or groups of constituents.

Exhibit VI-2
Summary Of Data Quality Levels

Data Quality Level	General Field Applications
1A: Qualitative Screening	General presence of contamination (*e.g.*, "Yes/no," low/medium/high); health and safety
1B: Semiquantitative Screening	Approximation of contaminated zone; provides order of magnitude estimations (*e.g.*, 10s, 100s, 1000s)
2: Quantitative Delineation	Delineation of specific contaminants
3: Quantitative Clean Zone	Regulatory monitoring, determining clean samples

Data Quality Level 1A: Qualitative Screening

DQL 1A is designated for initial screening of soil, soil gas, and groundwater by providing a "yes/no" indication of contamination. Measurements made with these methods may not always be consistent because of the lack of sample control and inherent method variability. As a result, clean samples cannot be determined from this level. Examples of DQL 1A methods include ambient air analysis or jar headspace using flame-ionization detectors (FIDs) and photoionization detectors (PIDs).

Data Quality Level 1B: Semiquantitative Screening

DQL 1B provides a rough, order of magnitude (*e.g.*, 10s, 100s, 1000s) estimate of contamination. It can be used for defining the location of known types of contamination. QA/QC procedures include a calibration curve generated using matrix spiked standards, regular calibration checks, and field blank/background samples. An example of DQL 1B is the data from some immunoassay test kit methods.

Data Quality Level 2: Quantitative--Delineation

DQL 2 methods provide reliable data for the delineation of contaminants during a site assessment. Typically, they are laboratory methods adapted for the field (*e.g.*, portable GC methods). DQL 2 methods:

- Measure individual constituents (*e.g.*, benzene) or groups of constituents (*e.g.*, BTEX, gasoline/diesel range organics);

- Produce data that are highly reproducible and accurate when appropriate QA/QC procedures are used; and

- Accomplish contaminant delineation, which may be correlated with a higher DQL method.

Data Quality Level 3: Quantitative--Clean Zone

DQL 3 methods are approved laboratory methods (*e.g.*, U.S. EPA SW-846 Laboratory Methods) and are intended to provide the most reliable data practicable. These methods can be used for confirming "clean" samples and for

regulatory monitoring. DQL 3 can be performed both off-site in a fixed laboratory or on-site in a mobile laboratory.

Field Analytical Method Descriptions

There are eight commonly available field analytical methods that can be used to detect petroleum hydrocarbons. Whenever any of these methods are used to determine the constituent concentrations, the use of appropriate standards is essential. There are two aspects to creating appropriate standards--using constituents that match as closely as possible the constituents (or type of contamination) found at the site and using the media (*e.g.*, soil, groundwater) that will be analyzed at the site. For example, if a silty soil contaminated with weathered gasoline is to be analyzed, free product found at the site may be used to spike a background sample of silty soil. If free product is not available, gasoline (from the local USTs) may be artificially weathered (*e.g.*, allow to sit in the sun for a period of time) and used to spike the silty soil.

The following text contains discussions of each method, including its operating principles, method descriptions, and method capabilities. At the end of each method discussion is a table of important selection criteria.

Detector Tubes

Detector tubes measure volatile gases and can be used for analyzing individual constituents or compound groups (*e.g.*, petroleum hydrocarbons). In addition to their frequent use for health and safety measurements, detector tubes can also be used as screening tools for volatile hydrocarbon contamination.

Operating Principles

Detector tubes are glass tubes that change color when exposed to specific gases. The glass tubes are sealed and filled with a porous solid carrier material which is coated with color reagents. The breakaway ends of the tube are snapped off and a known volume of air is drawn through the tube at a fixed flow rate using a hand or electric pump. As air passes through the tube, a stain is produced by the reaction of target constituents with the reagents inside the tube. The investigator reads the concentration from a scale on the tube. For most of the detector tubes that are used for hydrocarbon assessments, the length of the stain in the tube is proportional to the concentration of the constituent. In addition to visual observations, gas-specific measurements can be made using an optical analyzer.

Method Descriptions

Detector tubes provide a direct measurement of volatile hydrocarbon vapors in ambient air. They can also provide an indirect indication of soil and groundwater contaminant concentrations when used in field test kits for analysis of soil gas and headspace for liquids.

Ambient Air Measurements

Simple ambient air measurements can be made by inserting a detector tube into a hand pump or mounting it in an optical analyzer, drawing air through the tube, and reading the results. For hand-held pumps, readings can be taken in the ambient air directly above the soil or groundwater samples. Test kits are available for on-site identification and classification of ambient air above unknown liquids during an emergency response. Attachments are also available that allow for the testing of ambient air in monitoring wells or sumps.

Soil-Gas Test Kits

Soil-gas test kits allow for active soil-gas sampling and analysis with detector tubes. This method utilizes a probe that is driven into the soil to a desired depth. A detector tube is inserted into a sampling chamber near the tip of the probe and connected to the ground surface with an extension tube. After air is drawn through the detector tube, the probe is removed for reading. For a more complete discussion of active soil-gas sampling, refer to Chapter IV, Soil-Gas Surveys.

Liquid Test Kits

The liquid test kits consist of two types of headspace analyses: A bottle system where the liquid sample is aerated, partitioning volatiles from the liquid into the headspace; or a sealed sample bottle is agitated and the headspace is subsequently analyzed. The aerating test kit system utilizes a fretted bubbler tube fitted in a wash bottle containing the water sample that the investigator has measured to a specific volume. A known quantity of air is drawn through the bubbler to aerate the sample, volatilizing the constituents according to their Henry's law constant. The headspace then passes through detector tubes for analysis of the headspace in the bottle. The headspace concentration is correlated to a water concentration using calibration and temperature corrections. Exhibit VI-3 depicts a liquid extraction apparatus that can be used with detector tubes.

Exhibit VI-3
Detector Tube Liquid Extraction Apparatus

Rubber Hose

Detector Tube

Headspace

Gas Detector Pump

Carbon
Pretubes

250 ml Gas Washington Bottle

Fritted Bubbler
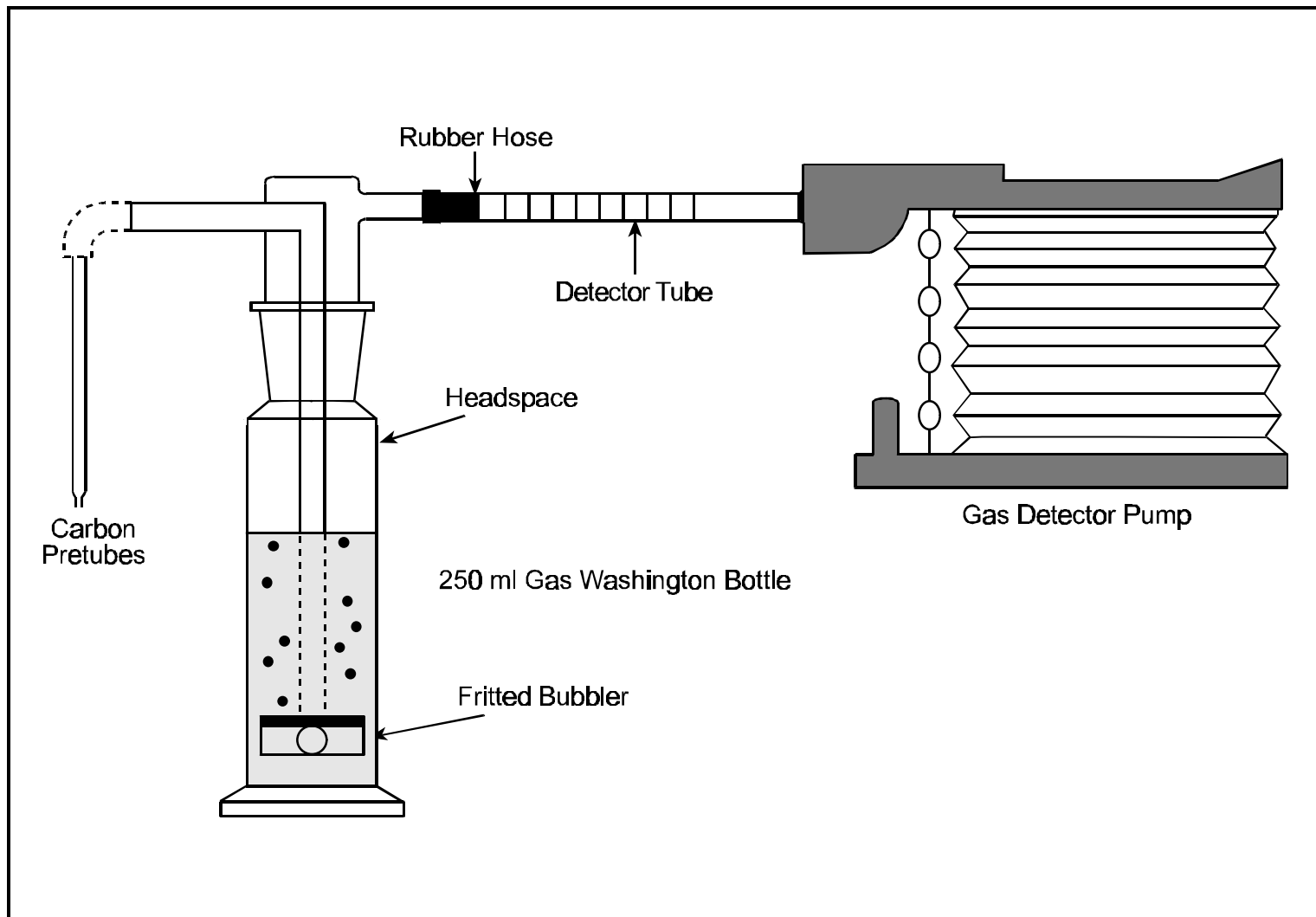
Source: U.S. EPA, 1990

Method Capabilities And Practical Considerations

Detector tubes are available for hundreds of compounds including many specific petroleum hydrocarbons and various general classes of petroleum hydrocarbons (*e.g.*, aliphatics). Detector tubes used in hydrocarbon analyses generally provide readings in the parts per million (ppm) range, although some can detect as low as 100 parts per billion (ppb). In addition, because detector tubes and pumps are precalibrated, the procedures are relatively easy to learn. Detector tubes provide DQL 1A information with ambient air and soil-gas test kit analysis. Because liquid test kit analysis is performed under more controlled conditions, detector tubes are able to provide DQL 1B information when used with this method.

A major limitation of this method is that the reagents in the detector tubes are generally cross-reactive with compounds of similar chemical behavior. Consequently, false positive and inaccurately high readings are possible. In addition, detector tubes can only be used in specific ambient temperature ranges as specified by the manufacturer. The minimum temperature is typically 32° F (0° C) and the maximum temperature typically ranges from 86° to 104° F (30° to 40° C). A summary of the capabilities and practical considerations for analysis using detector tubes is shown in Exhibit VI-4.

Fiber Optic Chemical Sensors

Fiber optic chemical sensors (FOCS) are used for *in situ* qualitative and semiquantitative measurements of volatile and semi-volatile hydrocarbons in groundwater and soil vapor. Some FOCS are used for detecting leaks of liquid and vapor-phase petroleum products. They can also be used for continuous monitoring of groundwater wells, soil vapor wells, and vapor extraction wells.

Operating Principles

FOCS use an optical fiber coated with a hydrophobic/organophyllic chemical to detect hydrocarbons. FOCS operate on the principle that the index of refraction of the optical fiber coating changes in direct proportion to the concentration of hydrocarbons in air or water. As hydrocarbons partition into the organophyllic coating, the change in the effective index of refraction can be determined by measuring the amount of light transmitted through the optical fiber. The response depends on the total number and type of hydrocarbons present. Exhibit VI-5 is a schematic drawing of FOCS operating principles.

Exhibit VI-4
Summary Of Detector Tube Method Capabilities
And Practical Considerations

	Ambient Air	Soil Vapor Test Kit	Liquid Test Kit
Compounds Detected	100s of specific compounds and compound groups including benzene, toluene, xylenes, gasoline, aliphatic hydrocarbons, MTBE, O_2, CO_2, and H_2S.		
Measuring Range	Varies with analyte. Most compounds can be detected in the ppm range, some as low as 100 ppb.		
Limitations	Cross reactivity may result in false positives or inaccurately high readings because many tubes are sensitive to chemically similar compounds (*e.g.*, benzene tubes also measure toluene to some degree). Minimum ambient air temperature is typically 32° F, maximum is typically between 86° and 104° F.		
Time For Analysis	2 to 5 minutes	10 to 15 minutes (includes probe placement)	5 to 10 minutes
Difficulty of Procedure	Low		
Data Quality Level	1A	1A	1B
Cost Per Sample[1]	$8	$27	$14

[1] Based on 100 analyses, includes cost of tube, pump, and test kit.

Method Descriptions

FOCS are typically used for the *in situ* measurement of groundwater monitoring wells and soil vapor wells. They can also be used to analyze the ambient air immediately above soil or for soil headspace analysis.

Water Wells

Before an analysis is performed, the probe sensor is cleaned and calibrated to zero in a solution of distilled water that is within 9° F (5° C) of the temperature of the well water. Calibrations are checked daily or periodically between samples

Exhibit VI-5
Schematic Drawing Of FOCS Operating Principles
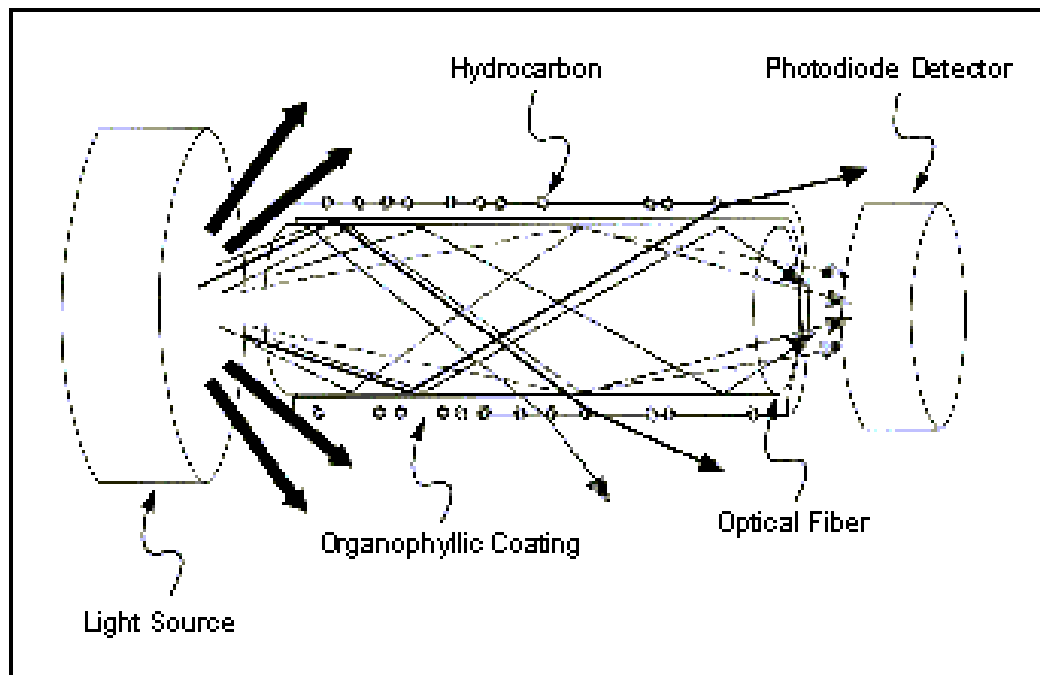
Source: Modified from ORS Environmental Systems product literature

using field standards or standards provided by the manufacturer (*e.g.*, p-xylenes, isopropanol).

To measure hydrocarbon concentrations in groundwater wells, the meter is set to measure continuously, and the probe is removed from the zero solution and lowered down the well to the desired depth. Readings are also affected by changes in temperature during analysis. If the well water temperature changes by more than 0.18° F (0.1° C) every 4 seconds, a 5-minute analysis is required to compensate for the temperature variations. Because results are site-specific, response factors are used to obtain specific constituent concentrations for specific wells with known contaminants (using a ratio of laboratory results to probe sensor results for a specific well being tested).

Vapor Wells

Before an analysis is performed, the probe sensor is cleaned, zeroed in a Tedlar bag with 5 liters of zero air (*i.e.*, air that contains less than 0.1 ppm total hydrocarbons), and calibrated using field standards or standards provided by the

manufacturer (*e.g.*, p-xylenes, isopropanol). Calibrations must be checked daily or periodically between samples.

To measure hydrocarbon concentrations in vapor wells, a humidity tube is used to zero the probe to the humidity in which the measurement will be made. The probe sensor is then lowered to the desired depth. When the readings have stabilized, the measurement can be recorded. The time required to reach a stable reading is related to the temperature difference between the temperature at which the probe sensor was zeroed and the temperature of the well. Well-specific response factors may be used to obtain a specific concentration for that well. After the measurement is completed, the probe must remain above ground for 5 minutes to allow any vapors in it to dissipate.

Method Capabilities And Practical Considerations

FOCS are capable of detecting VOCs and SVOCs with six or more carbon atoms. Thus, benzene (C_6) can be detected while methane (C_1) cannot. The response of the sensor probe is directly related to the quantity of hydrocarbons present in a sample, calibrated to a p-xylene response. However, highly soluble constituents yield a lower response than less soluble constituents. For example, benzene, which is approximately 10 times more soluble in water than p-xylene, responds with one-tenth the sensitivity of p-xylene. In addition, the response is affected by temperature. FOCS, therefore, almost always require temperature compensation, which is usually built into the sensor. The optimal temperature range of FOCS is generally between 50º and 86º F (10º and 30º C).

Because the readings provide a relative value, a response factor (empirically determined by the manufacturer) must be used to estimate contaminant levels once the constituents and their relative ratios have been determined. The strongest correlation of results with GC analysis comes either from a single well monitored over time or from wells contaminated by the same source. Exhibit VI-6 presents a summary of FOCS method capabilities and limitations.

Colorimetric Test Kits

Colorimetric test kits provide qualitative or semiquantitative screening of aromatic hydrocarbons in soil and water. They can generally provide information about compound groups (*e.g.*, BTEX, PAHs) but can also help determine concentrations of specific compounds. A portable spectrophotometer has recently been developed to aid in the evaluation of concentrations in samples, however, the

Exhibit VI-6
Summary Of FOCS Method Capabilities
And Practical Considerations

	Water	Vapor
Compounds Detected	VOCs and SVOCs $\geq$ C_6 (Benzene)	
Lower Detection Limits	0.1 to 5 ppm	3 to 65 ppm
Limitations	Does not measure specific constituents Concentrations at specific locations must be calculated by comparing historical DQL 3 results with FOCS results Free product saturates coating and exceeds meter scale Optimal temperature range is between 50° and 86° F.	
Time For Analysis	3 to 5 minutes	
Difficulty of Procedure	Low	
Data Quality Level	1A/1B	
Cost Per Sample[1]	<$1 to $10	

[1] Reflects the averaged cost over an extended period of time including consumables (*e.g.*, calibration standards) and the capital cost of equipment, ranging from $5000 to $6900.

primary method of evaluation is by visual comparison of sample results with calibrated photographs of specific substances (*e.g.*, gasoline, diesel fuel).

Operating Principles

Colorimetric test kits that are designed for hydrocarbon analysis create intensely colored aromatic compounds through the Friedel-Crafts alkylation reaction. This reaction utilizes a catalyst (*e.g.*, $AlCl_3$) to attach an alkyl group to an aromatic hydrocarbon (*e.g.*, benzene). In these test kits, an alkylhalide (*e.g.*, carbon tetrachloride [CCl_4]) is typically used as both an extracting agent for the hydrocarbons and as a reagent. Once the catalyst is added, the reaction proceeds. The resulting color (*e.g.*, orange, violet) provides information about the type of

constituent; the intensity of the color is directly proportional (within a specific range) to the concentration. Exhibit VI-7 presents a common Friedel-Crafts alkylation reaction utilized in colorimetric test kits.

Method Descriptions

Colorimetric test kits are available for soil and water analysis. The kits provide the reagents and equipment needed for the extraction and colorimetric analysis of aromatic hydrocarbons. Color charts, created from known concentrations of various constituents, are used for comparison with field results to determine the constituents and their approximate concentrations.

Water Test Kit

The water test kit requires the following steps:

- Pour the water sample into a separatory funnel;
- Add the solvent/extract (an alkylhalide) to the sample, agitate it, and wait until solvent/extract has settled to the bottom of the separatory funnel;
- Drain the extract into a test tube;
- Add the catalyst and agitate it while the reaction proceeds between the aromatics and the alkylhalide; and
- Compare the color of the sample in the test tube (precipitate) with the color chart standard.

Exhibit VI-7
Example Of Friedel-Crafts Alkylation Reaction Utilized
In Colorimetric Test Kits
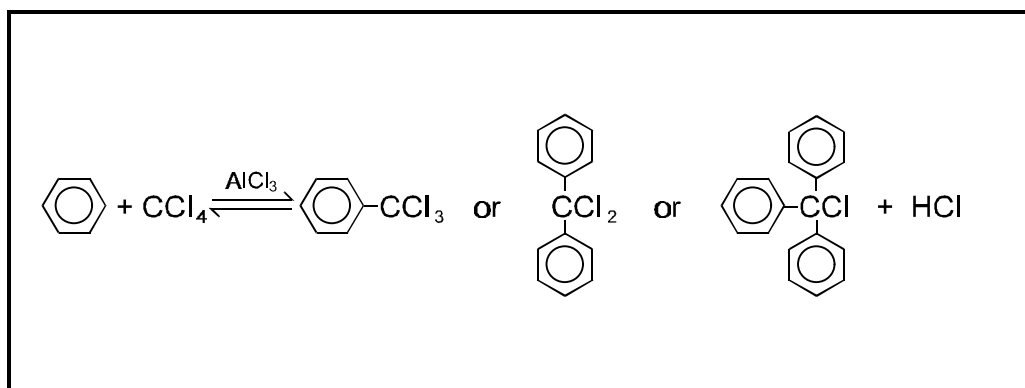
Soil Test Kit

The soil test kit requires the following steps:

- Measure a soil sample;
- Add the solvent/extract to the soil, agitate it vigorously, and wait for the solvent/extract to separate;
- Pour the extract into a test tube;
- Add the catalyst and agitate; and
- Compare the color of the sample in the test tube (precipitate) with the color chart standard.

Method Capabilities And Practical Considerations

Colorimetric test kits can be used to analyze aromatic hydrocarbons (with particular sensitivity to PAHs) in soil and water. In soil, the detection limit is generally in the 1 to 10 ppm range; in water it is less than 1 ppm. Colorimetric test kits are effective for analysis of gasoline, diesel fuel, and other fuel oil contamination. A particular advantage of this method is that it is not dependent on analyte volatility, making it especially useful for older spills and for heavier fuel oils.

One of the major limitations of the method is that when comparing samples with the color chart photos, constituent concentrations and colors (*i.e.*, type of constituent) can be difficult to determine when constituent concentrations are low. In addition, if the contamination is a mixture of constituents, lighter aromatics (*e.g.*, BTEX) which turn to shades of orange will be hidden by heavier constituents (*e.g.*, PAHs) which turn to shades of violet. As a result, constituents present in the sample should be known before analysis.

There are a number of potential interferences for this type of analysis. First, the presence of chlorinated solvents may result in false positive analysis with water or soil. Second, color interferences for organic-rich or clayey soils may make color interpretation difficult. Clay soils may also pose additional problems because the sample tends to clump, making contaminant extraction difficult. Finally, the reaction products are sensitive to UV radiation, becoming darker with time and causing the potential for overestimation of constituent levels. Constituents and concentrations should, therefore, be determined within 30 minutes of color formation.

A health and safety issue involved with the use of this method is that analysis of all water samples and soil samples with hydrocarbon concentrations less than 1000 ppm requires a heptane-carbon tetrachloride solution to be used for sample extraction. Therefore, reagents and waste products must be properly handled and disposed of after use, typically, they are shipped back to the manufacturer. For analysis of soil samples with greater than 1000 ppm hydrocarbons, a much more environmentally safe heptane solution (without tetrachloride) can be used for extraction.

Both soil and water test kits provide data for screening level analysis. Because the soil test provides variable response to a wide range of aromatic hydrocarbons, has several interferences, and can be difficult to use, it is classified as a DQL 1A analysis. The water analysis is more accurate and allows for an order of magnitude determination of contamination. As a result, it is capable of providing DQL 1B analysis. A summary of the capabilities and practical considerations for analysis using colorimetric methods is shown in Exhibit VI-8.

Analysis With Reflectance Spectrophotometer

A portable reflectance spectrophotometer and associated software have been developed that allow objective measurement of color intensity. Future innovations may allow quantification of specific constituents and increase the upper level of measurement. It is available for approximately $4,500.

Total Organic Vapor Analytical Methods With Flame Ionization And Photoionization Detectors

Total organic vapor (TOV) analytical methods detect the total volatile organic compounds in a sample. Although, they provide information about the relative magnitude of contamination, TOV methods are unable to distinguish specific compounds.

Operating Principles

There are two types of instruments commonly used in TOV analysis-- flame ionization detectors (FIDs) and photoionization detectors (PIDs).

Exhibit VI-8
Summary Of Colorimetric Test Kit Method Capabilities
And Practical Considerations

	Soil Test Kit		Water Test Kit	
Compounds Detected	Monoaromatic and polyaromatic hydrocarbons			
Measuring Range	Benzene	1 to 200 ppm	Benzene	0.2 to 10 ppm
	Toluene	0.5 to 250 ppm	Toluene	0.2 to 10 ppm
	Gasoline	1 to 1,000 ppm	Gasoline	0.5 to 20 ppm
	Diesel	1 to 1,000 ppm	Diesel	0.5 to 20 ppm
	JP-5	1 to 2,000 ppm	Naphthalene	0.1 to 2.5 ppm
Limitations	Mixtures of constituents may make colors difficult to distinguish without spectrophotometer. Investigators should know constituents present before analyzing samples UV light degrades the color of samples (*i.e.*, they become darker) approximately 30 minutes after color formation. Extraction of constituents may be difficult in clays. Organic and clay-rich soils may interfere with color. Carbon tetrachloride must be used, and properly disposed of, for analysis < 1000 ppm.			
Time For Analysis	10 to 20 minutes		10 to 15 minutes	
Difficulty Of Procedure	medium		low-medium	
Data Quality Level	1A		1B	
Cost Per Sample[1]	$17 to $42			

[1] Initial 30 analyses cost $42; subsequent analyses may cost as little as $17.

Flame Ionization Detectors

FIDs use a hydrogen flame to ionize organic vapors. The measured electrical current that is generated by the free ions, called the instrument response, is related to the concentration of volatile compounds present in the sample. While FIDs provide significant response to most organic vapors, they are more sensitive to aliphatic (or chained) hydrocarbons because these compounds burn more efficiently than aromatic (or ringed) hydrocarbons. FIDs are typically calibrated with methane.

Photoionization Detectors

PIDs use an ultraviolet lamp to ionize organic vapors. As with FIDs, the instrument response is related to the electrical current generated by the ionized compounds. Compounds with higher ionization potentials (*e.g.*, aliphatics) require more energy for ionization; therefore, the strength of the UV lamp determines the compounds that are ionized. UV lamps range in energy from 8.4 to 11.7 eV. Isobutylene is typically used as the calibration gas for PIDs. These instruments are most sensitive to aromatic hydrocarbons (*e.g.*, BTEX compounds), but some aliphatics can also be detected with the higher energy lamps.

Comparison Of Flame Ionization Detectors And Photoionization Detectors

In addition to the response differences to aliphatic and aromatic hydrocarbons, other factors to consider when selecting an FID or PID include the following.

- Response factors for specific constituents, which differ between types of instruments and among manufacturers, are important to know when calculating actual concentrations. For example, an FID calibrated with methane may respond 150 percent greater when exposed to the same concentration of benzene but the response may be only 25 percent for ethanol.
- FIDs remain linear from 1 to 1,000 ppm_v (parts per million by volume), and some can even reach 10,000 ppm_v; PIDs remain linear from 1 to 300 ppm_v, with some reaching 750 ppm_v under ideal conditions.
- Most PIDs are affected by high electrical currents (*e.g.*, power lines).
- PIDs can operate in conditions of high relative humidity and low O_2, but they require the calibration gas to approximate the test conditions. FIDs

can operate in humid condition, but low O_2, high CO_2, or windy environments will extinguish the FID flame.

- FIDs require more training than PIDs.
- FIDs require a source of ultra-pure hydrogen that may not always be available and requires special handling and shipping.
- PIDs are subject to false low values when methane (CH_4) concentrations are greater than 1 percent; FIDs have the opposite problem of being sensitive to methane and providing to false positive.
- Both instruments are adversely affected by low air flow and, although FIDs are more sensitive to slightly weathered gasoline (because of the presence of several aliphatics), neither is effective for detecting highly weathered gasoline, nor is either instrument accurate when ambient air temperatures are below 32° F (0° C).

Exhibit VI-9 provides a summary of the comparison between FIDs and PIDs.

Exhibit VI-9
Comparison Of FIDs And PIDs

	FIDs	PIDs
Compounds Detected	Aliphatic hydrocarbons (*e.g.*, butane, hexane), less sensitive (although significant response) to aromatics (*e.g.*, BTEX compounds)	Aromatic hydrocarbons and some aliphatics
Linear Range of Detection	1 to >1,000 ppm$_v$	1 to <300 ppm$_v$
Unfavorable Environmental Conditions	High CO_2, low O_2 (<15%), high winds, temperature below 32° F	High humidity (*e.g.*, 90%), >1% CH_4, low O_2 (<15%), temperature below 32° F
Miscellaneous Issues	Requires a hydrogen source Requires more training than PIDs High methane levels may be interpreted as contamination	Adversely affected by electrical power sources (*e.g.*, power lines and transformers) Methane can depress readings

Method Descriptions

TOV analytical methods provide an indirect indication of soil or groundwater contaminant concentrations by measuring the organic constituents that partition into the headspace. There are three general types of methods used with FIDs and PIDs--ambient air measurements, headspace screening, and headspace analysis. Each provides a varying degree of data quality.

Ambient Air Measurements

Ambient air measurements are performed by taking direct readings with either an FID or a PID in the air immediately above soil or groundwater samples. It is commonly used as a screening method to determine which soil or water samples should be analyzed with a higher data quality method. It is also used to help determine future sampling locations.

Headspace Screening

In order to perform a headspace screening, a soil or groundwater sample is placed in an airtight container, typically a glass jar or polyethylene bag, leaving one-half to one-third empty. The container is then either shaken, heated, or left to sit for a period of time in order to allow the hydrocarbons to partition into the headspace (*i.e.*, the air space above the sample). The headspace is then measured with an FID or PID. The use of a polyethylene bag allows for a steady sample flow rate to the instrument, however, hydrocarbons partitioning from the bag may affect the analysis so a blank sample should be tested and the results factored into the analyses.

This method involves a more controlled sample analysis than ambient air measurements. As a result, headspace screening provides more consistent readings that can be used for estimating relative concentrations. However, readings remain relatively inconsistent, because volatilization of contaminants is affected by:

- Soil type;
- Moisture content;
- Ambient air dilution into jar;
- Temperature variations; and
- Time to prepare and analyze sample.

Headspace Analysis

Headspace analysis is similar to headspace screening but the procedures are more controlled and the results more accurate. A measured quantity of a soil or groundwater sample is placed in a polyethylene bag. For soil samples, a specified volume of deionized water is also placed in the bag in order to facilitate a more consistent partitioning of organic vapors. The bag is then inflated and the sample is agitated. After a specified time, an FID or PID is used to measure the headspace. QC procedures include the development of a calibration curve using field standards. These standards help in the interpretation of instrument responses and provide a comparison with samples of known concentrations.

Method Capabilities And Practical Considerations

Ambient air measurements are classified as DQL 1A analysis because these readings are highly variable and little or no QA/QC is used with sample analysis. The lower detection limit is generally around 100 ppm_v but may be significantly lower under ideal conditions (*e.g.*, no wind, no humidity, high O_2 levels). Headspace screening measurements are also only qualitative and fall within the DQL 1A range, however, their detection limits are generally between 10 and 100 ppm. Headspace analysis is classified as DQL 1B, semiquantitative, method because it provides an order of magnitude indication of contamination, but it does not provide information about the concentration of specific constituents. The lower detection limit with this method may be as low as 0.1 ppm for gasoline in water, but it is generally above 1 ppm. For all three methods, soil samples that are clay rich or contain high organic content may provide inconsistent results. In addition, gasoline should be relatively fresh or only slightly weathered for useful results.

TOV analysis is one of the least expensive analytical methods available. A summary of the capabilities and practical considerations of these three analytical methods using an FID or PID is summarized in Exhibit VI-10.

Turbidimetric Test Kits

Turbidimetric test kits are used for measuring the total petroleum hydrocarbon (TPH) content in soil. These test kits provide quantitative screening of soils for the presence of mid-range petroleum hydrocarbons (*e.g.*, diesel fuel, fuel oils, grease). Turbidimetric test kits can be used to identify source areas of contamination in the vadose zone. This method is also being adapted for analysis of TPH in water and may soon be commercially available.

Exhibit VI-10
Summary Of Total Organic Vapor Method Capabilities
And Practical Considerations

	Ambient Air	Headspace Screening	Headspace Analysis
Compounds Detected	FIDs: Aliphatics (*e.g.*, butane), less sensitive to aromatics (*e.g.*, BTEX)		
	PIDs: Aromatics, some aliphatics		
Lower Detection Limits			
Gasoline in water	>100 ppm	10s to 100s ppm	0.1 to 1 ppm
Gasoline in soil	>100 ppm	10s to 100s ppm	1 to 10 ppm
Diesel in soil	>100 ppm	100s ppm	10s to 100s ppm
Limitations	Clay-rich or high organic content may provide inconsistent results. Best used with relatively fresh or only slightly weathered gasoline.		
Time For Analysis	2 minutes	10 to 30 minutes	10 to 30 minutes
Difficulty Of Procedure	low	low	medium
Data Quality Level	1A	1A	1B[1]
Cost Per Sample[2]	< $1	$1 to $5	$10

[1] Only if constituents are predetermined.
[2] Equipment costs are typically between $4,000 and $8,000.

Operating Principles

Turbidimetric soil test kits indirectly measure the TPH in soil by suspending extracted hydrocarbons in solution and then measuring the resulting turbidity (*i.e.*, the relative cloudiness of a solution) with a turbidity meter. The suspending solution causes extracted TPH to separate out of solution (*i.e.*, precipitate) while remaining suspended. Because the concentration of petroleum hydrocarbons in the soil is directly proportional to the turbidity measurement, a standard calibration curve can be developed to estimate TPH.

Method Description

Turbidimetric soil test kits utilize extraction solvents, analytical reagents, and a portable turbidity meter to determine contamination levels. The three steps in the test are as follows.

- Extraction: A methanol-based (chloroflorocarbon-free) solvent is used to extract hydrocarbons from the soil sample. The sample is then agitated, and the soil is allowed to settle.

- Filtration: The extract is then separated from the soil with a filter and placed in a vial with a developing solution.

- Analysis: When the developing solution equilibrates, a reading is taken with the turbidity meter. The turbidity value is proportional to the amount of petroleum hydrocarbons present.

The constituents should be identified before using this method so that a response factor can be selected from a reference table provided by the manufacturer. The meter can be calibrated using an extraction solvent vial as a blank and the calibration standard provided with the kit. Samples can be run individually or batched. Optimum performance and throughput are accomplished by running groups of 10 samples along with a blank and a standard.

Method Capabilities And Practical Considerations

Turbidimetric test kits are primarily used to screen petroleum hydrocarbons in soil. The method, which is sensitive to heavier molecular weight hydrocarbons (*e.g.*, diesel fuel), is capable of detecting C_{12} to C_{30} hydrocarbons with greatest sensitivity at the high end of the range. Turbidimetric soil test kits provide results in the part per million (ppm) range. Organic-rich soils may limit the effectiveness of the extraction or cause a positive interference. Background levels outside the zone of contamination can be used for a correction of results. The effective temperature range of this method is between 40° and 113° F (4° to 40° C). In addition, high moisture content in the soil sample may dilute the concentration of hydrocarbons in the extract resulting in negative interference. A summary of turbidimetric method capabilities and practical considerations is presented in Exhibit VI-11.

Exhibit VI-11
Summary Of Turbidimetric Method Capabilities
And Practical Considerations

	Soil Test Kit
Compounds Detected	It is most sensitive to "middle" chain hydrocarbons (*e.g.*, C_{12} to C_{30}), including diesel fuel and kerosene.
Measuring Range	Diesel 13 to 2000 ppm
	Used Motor Oil 19 to 2000 ppm
Limitations	Light-weight petroleum hydrocarbons (*e.g.*, gasoline) are not detected. Organic-rich soil may limit the effectiveness of the extraction or cause positive interferences. High soil moisture content may cause negative interferences. Filtration may be difficult with clay soils. Effective temperature range is 40° to 113° F.
Time For Analysis	15 to 20 minutes
	25 samples per hour when batched
Difficulty Of Procedure	Low-Medium
Data Quality Level	1B
Cost Per Sample[1]	$10 to $28

[1] Initial 30 analyses cost $28; subsequent analyses may cost as little as $10.

Immunoassay Test Kits

Immunoassay test kits can be used to measure petroleum hydrocarbons in soil and water. Test kits may measure groups of compounds (*e.g.*, short chain hydrocarbons, TEX) or a general assay range (*e.g.*, PAHs, TPH). Although they provide quantitative screening information, immunoassay test kits can determine if samples are above or below an action level (*i.e.*, whether a sample is "clean").

Operating Principles

Immunoassay test kits use antibodies (*i.e.*, proteins developed by living organisms to identify foreign objects as part of their immune systems) to identify and measure target constituents (*i.e.*, antigens) through the use of an antibody-antigen reaction. Antibodies are very useful for identifying specific compounds because they have binding sites that are designed to preferentially bond to specific antigens, as depicted in Exhibit VI-12. This technology has been used for decades by the medical industry.

In order to facilitate analysis, immunoassay test kits utilize special reagents, called enzyme conjugates, to allow for color development. Enzyme conjugates, as depicted in Exhibit VI-12, are a combination of molecules of the constituent of interest attached to specialized enzyme molecules. During analysis, the enzyme conjugate and the sample are mixed with the antibodies at

Exhibit VI-12
Schematic Drawings Of Antibody And Enzyme Conjugate
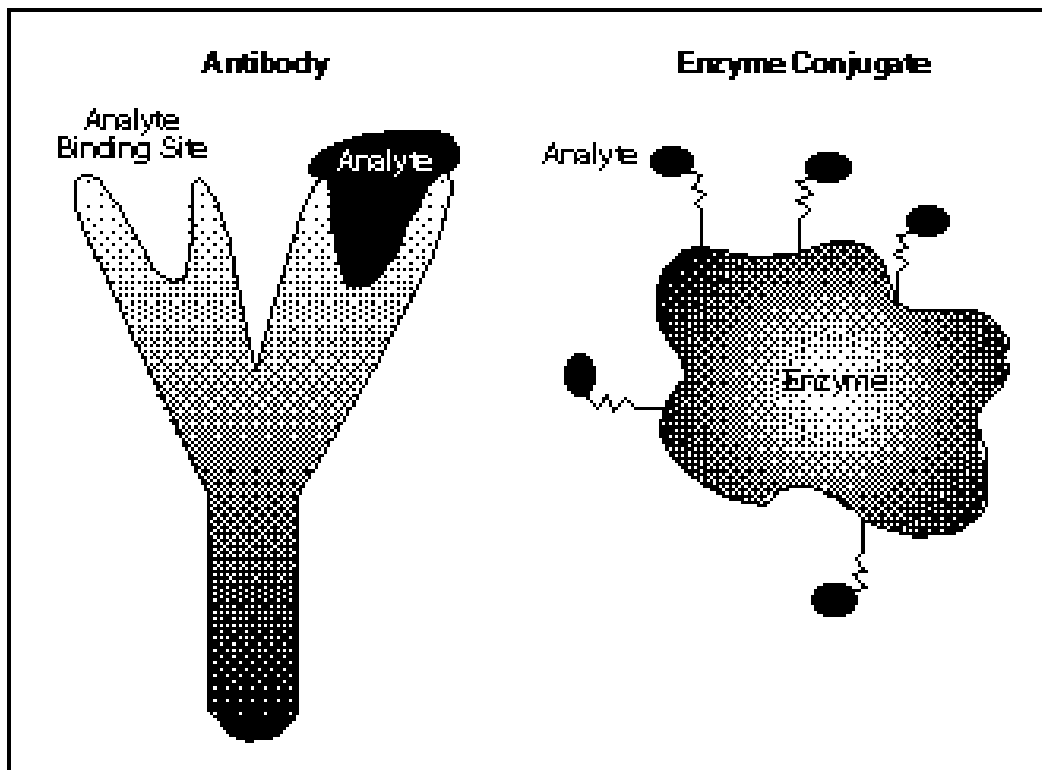
Source: ENSYS Environmental Products, Inc.

approximately the same time causing them to compete for binding sites on the available antibodies. When the constituents of interest have had time to bind to the antibodies, the system is washed and a substrate solution is added. This solution reacts with any enzyme conjugate that remains bound to the antibodies, producing a color. As a result, for most immunoassay test kits, the color is inversely proportional to the contaminant concentration (*i.e.*, the darker the color, the lower the concentration). The final concentration can be determined by comparing the color developed in the sample with that of a reference standard, either visually; with a portable photometer; or with an optical reflectance meter.

Method Descriptions

Although the procedures developed by the manufacturers of immunoassay test kits may vary, a number of steps can be outlined. Methods are available for both water and soil analysis. Water samples are analyzed directly, but soil samples require an extraction process that results in an indirect analysis.

Test kits are used for semiquantitative screening. This procedure involves setting an action level and observing whether the contaminant concentration is above or below that level. Multiple action levels can be set to place the sample within a discrete range (*e.g.*, above 100 ppm but below 500 ppm). Multipoint calibration curves can be used to further define concentrations (*e.g.*, above 200 ppm but below 250 ppm). These calibration curves are generated using standards that are provided by the manufacturer. Multiple analyses can be run in batch assays for both types of test kits. Standards and blanks are run with each batch.

Water Test Kits

To perform a water analysis:

- The water sample is placed in a reaction cell or test tube that contains the analyte-specific antibodies;
- An enzyme conjugate is added;
- After a specific period of time has passed, the sample is then washed, leaving behind analyte and/or enzyme conjugate bound to antibodies;
- The color development reagents (*i.e.*, substrate solution) are added and allowed to incubate;
- A stop solution is added; and
- The contaminant concentration is evaluated.

Soil Test Kits

Soil test kits utilize the same steps as water test kits except they have additional steps involved in extraction of analytes. The soil test kit analysis steps are as follows:

- An alcohol-based solvent (typically methanol) is added to the soil sample to extract the contaminant;
- The mixture is agitated to disaggregate the soil and extract the contaminants;
- The soil extract is placed in a reaction cell or test tube containing antibodies;
- The enzyme conjugate is added; and
- The remaining part of the test is conducted like the water test described above.

Method Capabilities And Practical Considerations

Immunoassay test kits are available for both water and soil analysis of short chain hydrocarbons (TEX), PAHs, and petroleum fuels (TPH). Tests can be performed for DQL 1B screening, however, constituent concentrations can be determined to be lower than a set action level with a high degree of certainty within a test kit's detection limit. As a result, they can be used for determining "clean" samples. In general, immunoassay test kits are best suited for analyzing short and middle chain hydrocarbons (<7 ring aromatic compounds and $<C_{11}$ aliphatic compounds). They are not effective for analyzing lubricating or hydraulic oils. Lower detection limits for petroleum analyses in water are generally in the ppb range and for soil in the ppm range. Upper detection limits are not provided because samples with high constituent concentrations can be diluted to a measurable range.

A number of issues affect the interpretation of immunoassay test kit results and should be clarified.

- Immunoassay test kits are designed to test for specific analytes or range of analytes; these kits are not capable of measuring a category as broad as all petroleum hydrocarbons. As a result, TPH tests do not measure every constituent present in fuel.
- Cross-reactivity occurs and may result in false positives. For example, an assay designed to detect TEX may give a positive result in the presence of a high concentration of PAHs (*e.g.*, naphthalene). The cross-reactivity

data for many hydrocarbon constituents and mixtures are available from the manufacturer; this information is important in interpreting test results.

- "BTEX" test kits actually measure a broad range of short-chain hydrocarbons because benzene is difficult to detect. These test kits give results that correspond with TEX concentrations for gasoline constituents and are designed for selectivity to xylenes with varying sensitivity for other aromatics.

- Immunoassay test kits must be used within each manufacturer's specified temperature range, which is generally between 40° and 90° F (4° and 32° C) and must be stored under conditions specified by the manufacturer (ranging from refrigeration at 40° F to room temperature). In addition, these kits must be used before the expiration date to provide valid data.

There are two problems that are specific to soil analysis. First, organic and clay-rich soils may limit the effectiveness of soil extraction and require longer extraction times than other soil types. Second, field extraction of PAHs may be less effective than the extraction methods used in the laboratory, and excessive amounts of oil in soil samples will interfere with the analysis of PAHs. Exhibit VI-13 presents a summary of immunoassay test kit method capabilities and practical considerations.

Portable Infrared Detectors

Portable infrared (IR) detectors measure the total petroleum hydrocarbons (TPH) in soil and water samples. Field methods involve a modification of U.S. EPA Method 418.1 or U.S. EPA SW-846 Method 8440 (U.S. EPA, 1997). IR detectors are most effective for mid- to heavy-range hydrocarbons.

Operating Principles

Portable IR detectors are spectrophotometers that measure the absorbance of IR radiation as it passes through sample extracts. The method operates under the principle that the hydrogen-carbon bond of petroleum hydrocarbons will absorb IR radiation at specific wave lengths, typically between 3.3 and 3.5 microns. Once contaminants are extracted from water or soil samples, absorption measurements can be directly related to TPH concentrations through the use of appropriate calibration standards.

Several petroleum hydrocarbons are shown in Exhibit VI-14. The top graph presents the IR spectra for two aliphatics--hexane and hexadecane; the

Exhibit VI-13
Summary Of Immunoassay Test Kit Method Capabilities
And Practical Considerations

	Water Test Kit	Soil Test Kit
Compounds Detected	• Short chain hydrocarbons (TEX) • PAHs • TPH	
Lower Detection Limit	TEX 100 ppb PAHs 10 ppb TPH 100 ppb	TEX 2 ppm PAHs 1 ppm TPH 5 ppm
Limitations	Antibodies may cross react with petroleum contaminants not targeted. Kits must be used between 40° and 90° F. Kits may be damaged if frozen or exposed to prolonged heat. Organic and clay-rich soil may limit effectiveness of extraction (soil kits only) . Field extraction of PAHs with methanol is not as rigorous as laboratory extraction (soil kits only).	
Time For Analysis	30 to 45 minutes	
	8 tests per hour when running batches	5 tests per hour when running batches
Difficulty of Procedure	Medium	
Data Quality Level	1B	
Cost Per Sample[1]	$20 to $60	

[1] Cost decreases with greater number of samples

bottom graph presents the IR spectra for several aromatics--benzene, toluene, xylene, and chlorobenzene. The concentration for all these constituents is approximately 500 ppm, except for hexane which is about 250 ppm. Note that peak response for the aliphatics is at wave lengths of approximately between 3.4 μm and 3.5 μm. The peak response for the aromatics is approximately between

Exhibit VI-14
Infrared Spectra For Selected Aliphatic And Aromatic
Hydrocarbons
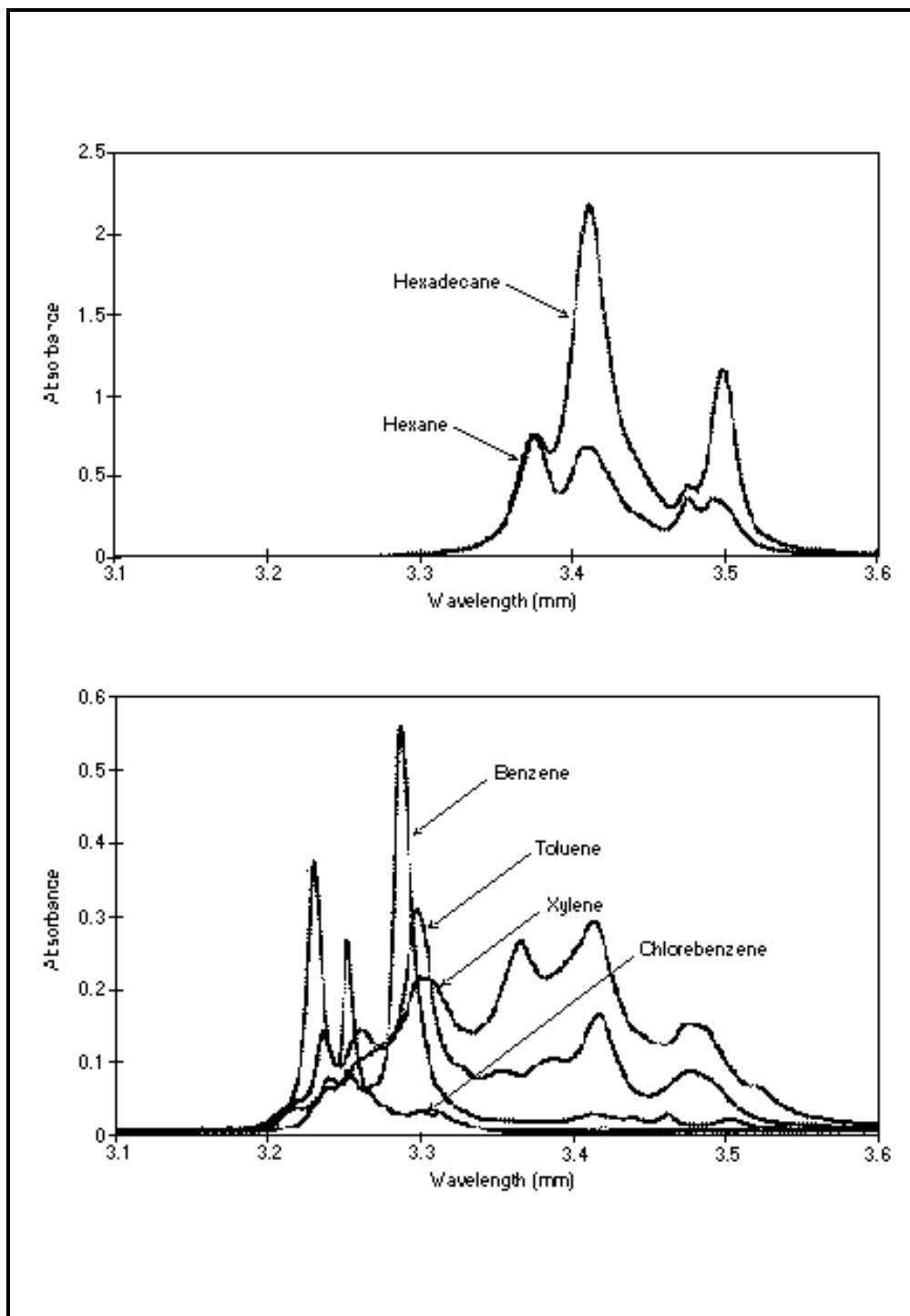
Source: General Analysis Corporation

wavelengths of 3.3 μm and 3.4 μm. Also note that the absorbance scale is different for aliphatics and aromatics, the aliphatics absorbance is much greater and, as a result, measurements may be biased toward them.

Method Description

Analysis of petroleum hydrocarbons with portable IR detectors requires that calibration standards be developed so that sample measurements can be correlated to actual concentrations. Calibration standards are preferably made with the constituents that are present at the site. If necessary, reference standard specified in U.S. EPA Method 418.1 may also be used, but this standard is best suited for the measurement of aliphatic hydrocarbons and it will give only approximate values.

For analysis of soil, samples must first be chemically dried by adding anhydrous sodium sulfate. For both soil and water samples a solvent that will not interfere with the analysis is added for extraction of hydrocarbons and manually shaken for a period of time. Method 418.1 uses Freon-113™ (1,1,2-trichloro-1,2,2-trifluroethane). The SW-846 method utilizes supercritical CO_2 for extraction into perchloroethane (PCE). Analysis can then be completed with Method 8440. Field extraction procedures generally consist of a single extraction while laboratory procedures typically consists of at least three extractions. A silica gel should then be added to remove polar nonpetroleum hydrocarbons (*e.g.*, esters and fatty acids) that can cause false positives. The extract is then poured into a quartz curvette for measurement with the infrared spectrophotometer.

Method Capabilities And Practical Considerations

Infrared spectroscopy is useful for measuring the TPH of hydrocarbons in the C_6 to C_{26} range, however, results are biased toward hydrocarbons greater than C_{12} because of their greater response to IR, and because larger hydrocarbons volatilize less during extraction. As a result, it is not effective for measuring VOCs. In addition, responses are typically biased toward aliphatic hydrocarbons because of their larger response to IR when wave lengths between 3.4 μm and 3.5 μm are used. If wave lengths around 3.3 μm are used, aromatic hydrocarbons can also be measured with minimal interference from aliphatics as long as compounds are known and appropriate standards are used. Detection limits are approximately 2 ppm for soil analysis and 0.08 ppm for water analysis.

Another limitation of this method is that results can not be correlated with health or environmental risks because all hydrocarbons are grouped together and presented as one number. Positive results may be related to compounds found

naturally in organic and clay-rich soils, or in petroleum products, which are not carcinogenic. As a result, although they give results at DQL 2, IR data require correlation with constituent specific methods as well (*e.g.*, GC analysis).

In addition, there are also a number of natural interferences with this method. Soil type is an important consideration because the extraction efficiency is much higher in sands than in clays. Furthermore, although most non-petroleum hydrocarbons can be removed by silica gel treatment, terpenes, which are found in conifers, citrus oils, and eucalyptus are not removed and can cause false positives.

The operational temperature range of IR spectroscopy is generally between 40º and 104º F (4º and 40º C) but may vary between manufacturers. The difficulty of this procedure is medium compared with other field methods. The cost and the time of analysis depend primarily on the number of extractions used per sample and the soil type (because clays require a longer extraction time). Each extraction takes about 5 minutes; analysis time is less than one minute. Exhibit VI-15 presents a summary of IR spectroscopy method capabilities and limitations.

Field Gas Chromatographs

Field gas chromatographs (GCs) are used for constituent-specific analysis of soil, soil-gas, and water samples for volatile and semi-volatile hydrocarbons. They have the capability to provide the highest data quality of all commonly used field analytical methods.

Operating Principles

Gas chromatographs are comprised of two major components: A column that separates individual constituents and a detector that measures the signal response of constituents. The column is a long, thin, coiled tube. An inert carrier gas (*e.g.*, hydrogen, helium, nitrogen, or zero air) is used to transport constituents through the column. Because compounds with low molecular weights and high volatility travel through the column faster than heavier compounds with low volatility, the constituents of a sample separate through the distance of the column. Discrimination of constituents is often difficult if two or more compounds exit the column at the same time (*i.e.*, coelute). The likelihood of compounds coeluting decreases with increasing column length.

A detector is located at the end of the column. For hydrocarbon investigations, the most applicable detectors are PIDs and FIDs. The design of PIDs and FIDs is modified slightly for GC analysis, allowing for greater detection

Exhibit VI-15
Summary Of Infrared Spectroscopy Method Capabilities
And Practical Considerations

	Soil Analysis	Water Analysis
Compounds Detected	C_6 to C_{26} range hydrocarbons	
Detection Limit	2 ppm	0.08 ppm
Limitations	Lighter petroleum hydrocarbons (*e.g.*, BTEX) are not accurately detected because of their volatility. Results are biased toward medium and heavy hydrocarbons compounds (*i.e.*, $\geq C_{12}$) unless appropriate standards are used. Extraction efficiency in clays may be lower than in other soil types. Organic and clay-rich soils may result in false positives unless appropriate standards and IR wavelengths are used because many non-petroleum hydrocarbons (*e.g.*, terpenes) are also extracted and analyzed. Health and environmental risks are difficult to determine from TPH levels. Operating temperature range is generally between 40° and 104° F.	
Time For Analysis	5 to 20 minutes	
Difficulty Of Procedure	Medium	
Data Quality Level	2	
Cost Per Sample	$5 to $30	

limits. The detector responses are displayed on either a chart recorder or a computer screen to form a chromatogram (*i.e.,* the detector reponses plotted against retention time for a sample). The integrated area under each response peak is proportional to the concentration of that constituent. Constituents are identifed through a comparison of retention times with standards. Exhibit VI-16 is an example of a chromatogram created by a portable GC.

Exhibit VI-16
Example Of A Portable GC Chromatogram
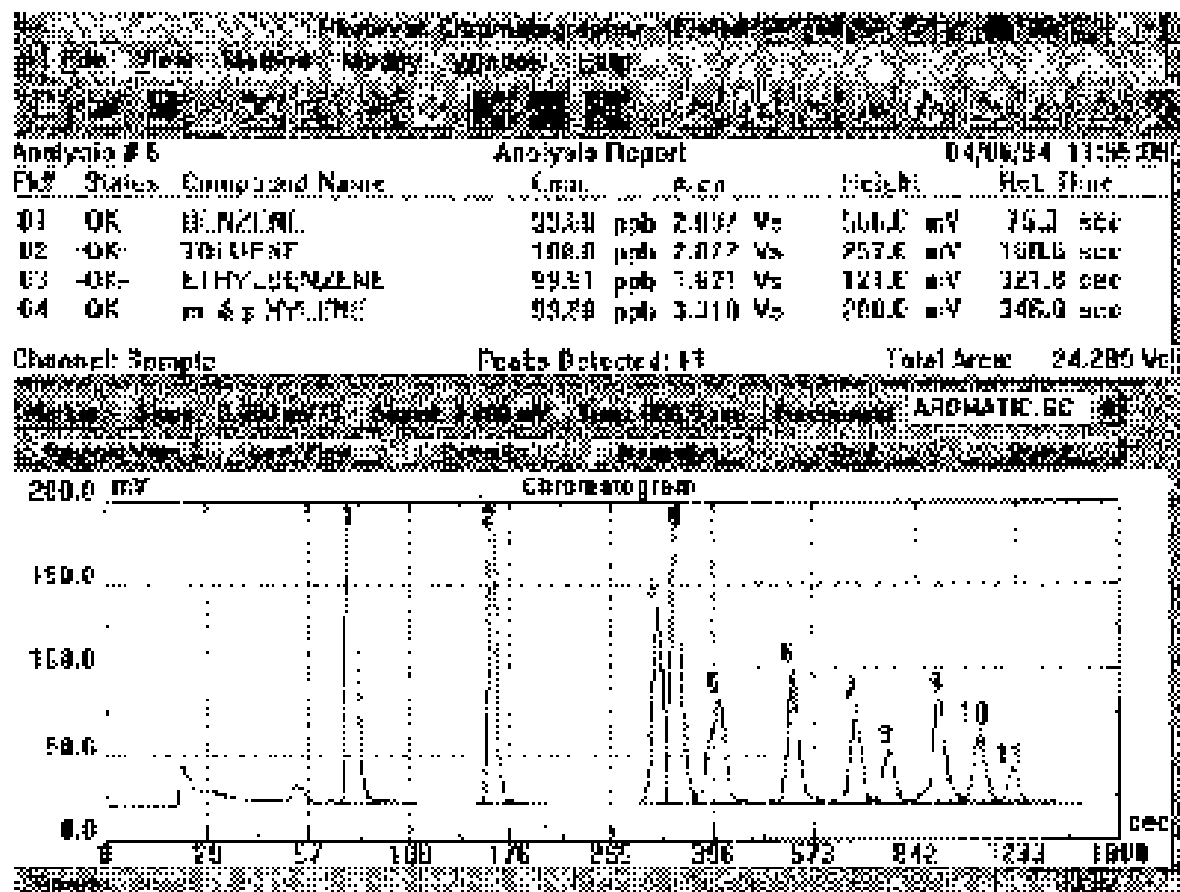
Source: U.S. EPA, 1995

There are two types of field GCs currently used for assessing petroleum releases--portable and transportable. Both types utilize the same basic operating principles, however, their capabilities differ and, as a result, so do their applications.

Portable GCs

Portable GCs are durable, compact, and light weight. Portability is possible because these GCs are equipped with internal batteries and carrier gas supplies. These features, however, limit the available energy supply that is needed for rapid temperature ramping (*i.e.*, heating) of the column. Instead, portable GC columns are heated isothermally.

Transportable GCs

Transportable GCs are typically mounted in a mobile laboratory, but because they require external power and gas supplies, they are not portable. Most transportable GCs are capable of rapid temperature ramping of the column, and many transportable GCs can be certified to perform U.S. EPA, SW-846 methods. As a result, they can provide data in the field that are equivalent to the data generated by certified fixed laboratory GCs.

Comparison Of Portable And Transportable GCs

The primary advantages of portable GCs are that they are easily carried into the field and that the time they require for analysis is generally shorter than for transportable GCs. Analysis with portable GCs is generally less than 10 minutes while transportable GCs commonly require 10 to 40 minutes (although 60 minutes may be required for some methods). Portable GCs tend to use PID detectors because hydrogen gas is not required. As a result, many aliphatic compounds cannot be detected with this equipment.

The primary advantage that transportable GCs have over portable GCs is that transportable GCs are capable of providing better constituent separation and, therefore, more accurate identification and quantitation of constituents. Greater separation of constituents is possible because transportable GCs generally use longer capillary columns than portable GCs (10 to 15 meters versus 30 to 60 meters). In addition, rapid temperature ramping of transportable GC columns and consistent temperature control of the entire GC system provides better separation and reproducibility than the isothermal heating of portable GCs.

Transportable GCs are available with a variety of detectors, including PIDs and FIDs.

Method Description

Field GCs are capable of performing soil, soil-gas, and water analyses. Soil-gas samples are the simplest to analyze because they do not require sample preparation. Soil and water samples, however, require preparation of which a couple of options are available.

Soil-Gas Analysis

Soil-gas samples are collected as described in Chapter IV, Soil-Gas Surveys. Analysis can be performed with GCs through direct injection of the sample by two methods. A microliter syringe or a loop injector (*i.e.*, a sample container that has been adapted for automatic injection via a pump internal to the GC) can be used.

Soil And Water Analysis

There are generally three methods used for analyzing soil and water samples for petroleum hydrocarbons with GCs. The simplest method is static headspace which is used for analysis of VOCs with both portable and transportable GCs. Solvent extraction is also used with both portable and transportable GCs. It is commonly used for SVOCs. The more complicated, time-consuming method called "purge and trap," is most effective for VOCs and is typically not performed with portable GCs because the energy requirements are excessive.

Static Headspace

The static headspace method is described in SW-846 Method 5021 (EPA, 1997). A version of this method has been modified for use by portable GCs. Static GC headspace analysis of water involves placing an aqueous sample in a sealed septum vial (analysis of a soil sample involves placing soil in a septum vial with analyte-free water), agitating, and then placing the sample in a water bath at constant temperature. Volatile hydrocarbons from the sample partition into the headspace, eventually reaching equilibrium. The concentration of volatile hydrocarbons in the headspace is representative of the concentration of dissolved

volatiles in the water. An aliquot of the headspace is then withdrawn from the vial with a gas-tight microliter syringe and injected directly into the GC column.

Solvent Extraction

The solvent extraction method provides higher hydrocarbon recovery than the static headspace method for SVOCs.   A specified mass of soil is dispersed in an organic solvent which partitions the hydrocarbons into the solvent (*e.g.*, pentane). The solvent can then be introduced into the GC by using direct injection.

Purge And Trap

The purge-and-trap method provides higher hydrocarbon recovery and lower detection limits than the static headspace method. It is conducted with transportable GCs because of the high energy requirements. Prepared samples are sparged with an inert gas (usually helium) in a purge chamber at ambient temperature causing volatile hydrocarbons to be transferred from the aqueous to the vapor phase. The vapor passes through an adsorbent trap that strongly retains selective hydrocarbon constituents. The sorbent is then heated to release hydrocarbon constituents and an effluent sample is directly transferred into the GC column for analysis.

Method Capabilities And Practical Considerations

Field GCs provide quantitative, constituent-specific analysis of volatile and semi-volatile hydrocarbons. In particular, field GCs can resolve key constituents for evaluating risk and determining corrective action criteria. Field GCs can measure constituent concentration in the part per billion (ppb) range for soil, soil-gas, and water with a lower detection limit of between 1 to 10 ppb, depending on the method and equipment. Samples with concentrations of less than one thousand ppb can be analyzed without dilution. GC analyses are the primary method for determining "clean zones" when delineating contamination. They also be used to identify the type of hydrocarbon/fuel contamination (*e.g.*, gasoline, diesel fuel). In addition, they are the only available field method for determining MTBE concentrations.

Limitations of field GCs include the following:

- Variations in temperature must be minimized and ambient air must not be contaminated.
- Analytical schemes for field GCs are usually not set up to measure low volatility and nonvolatile hydrocarbons (*e.g.*, crude oil).
- A wide range of hydrocarbons (*e.g.*, gasoline to fuel oil) are typically not measured in a single analysis.
- Highly contaminated samples may require dilution to prevent them from exceeding the maximum calibration range of the detector.
- Nontarget constituents may interfere with peak resolution if they have similar retention times or coelute with the target compounds. If many interfering peaks are present, the separation may not be adequate to determine constituent concentrations. In this case, total chromatogram integration can be used to determine the total VOCs.
- A greater level of operator training is required for field GCs than with other field analytical methods. Although portable GCs may require less training than transportable GCs, both methods typically require a chemist or someone with significant chemistry training.

DQLs are dependent on the analytical method, the QA/QC procedures, and the equipment capabilities. In addition, differences in the construction of portable and transportable GCs (*e.g.*, column heating, column length, temperature control) control the attainable DQL. Portable GCs are capable of providing DQL 2 information, and transportable GCs may provide DQL 3 data. Exhibit VI-17 presents a summary of field GC method capabilities and limitations.

Exhibit VI-17
Summary Of Field GC Method Capabilities
And Practical Considerations

	Water	**Soil**	**Soil-Gas**
Compounds Detected	Constituent-specific volatile/semivolatile hydrocarbons		
Lower Detection Limits	1 to 10 ppb		
Limitations	Does not measure wide range of hydrocarbons in a single analysis (*e.g.*, gasoline to fuel oil). Samples >1000 ppb may require dilution to prevent exceeding maximum range of detector. Non-target compounds that coelute with target compounds will cause a positive bias in the interpretation of results. Operation affected by extreme temperature and contaminated working environments. Requires high degree of training.		
Time For Analysis	Portable: <10 minutes		
	Transportable: 10 to 60 minutes depending on constituents and method		
Difficulty Of Procedure	Medium-High	High	Medium
Data Quality Level	Portable 2		
	Transportable 2/3		
Cost Per Sample	Portable $20 to $50		
	Transportable $50 to $70		

Several new field analytical methods are currently available for use in expedited site assessments. They are classified as emerging because they are recent developments and/or they are undergoing rapid change. Accordingly, information in this text is not presented in as much detail as in the previous section because details may soon become outdated. These methods include two types of GC/mass spectrometry (MS) and three types of *in situ* sensing methods that are used in conjunction with direct push technologies described in Chapter V.

Gas Chromatography/Mass Spectrometry

Gas chromatography/mass spectrometry (GC/MS) systems operate under the same principles as the field GCs, but instead of using a PID or FID as the detector, they use a mass spectrometer. Because MS records constituent specific mass spectra (*i.e.*, a spectrum of molecular fragments produced from the ionized parent compound, that is resolved according to the mass-to-charge ratio), it allows for identification of specific compounds.

GC/MS systems have been available in fixed laboratories for many years. Recently, portable and transportable GC/MS has been developed. These systems are typically not needed at UST sites because the types of contaminants are generally known. In addition, it is inappropriate for TPH analysis. If, however, chlorinated hydrocarbons migrate onto the site, or confirmation of specific constituents is necessary, GC/MS may be appropriate. GC/MS detectors are no more sensitive than GC/PID or GC/FID detectors, and they can be less sensitive for certain analytes.

Portable GC/MS

Portable GC/MS systems have been designed primarily for air monitoring, but they can also be used for headspace analyses. They are equipped with internal batteries and carrier gas supplies. Because of these features, portable GC/MS systems (as with portable GC/PIDs) have a limited energy supply and, consequently, operate isothermally. In addition, these features also limit the types of constituents that can be analyzed.

Transportable GC/MS

Compared with laboratory-grade systems, transportable GC/MS systems are smaller, more rugged, lighter in weight, and use less power. Typically, GC/MS systems have been used to analyze chlorinated contaminants. GC/MS methods can be used to confirm and delineate the leading edges of contaminant plumes and to verify contaminants suspected with GC/PID/FID (*e.g.*, MTBE). EPA Methods 624 and 8260 (VOCs) and 8270 (SVOCs) can be performed using transportable GC/MS systems. In general, GC/MS systems are well-suited for analyzing a broad range of constituents, especially heavier molecular weight constituents (*e.g.*, PAHs) which are not as easily resolved by GC methods alone.

In Situ Analysis Using Direct Push Technologies

Several methods have recently been developed for the *in situ* analysis of petroleum hydrocarbon contamination using direct push (DP) probes. They are typically used in conjunction with several other sensors (*e.g.*, soil conductivity, temperature, friction/resistance) to provide detailed, objective logging information. These measurements provide screening level information about the presence of contamination while at the same time logging soil for various parameters including soil type and depth to groundwater.

There are three emerging methods currently available for *in situ* analysis with DP systems--laser-induced fluorescence (LIF), fuel fluorescence detectors (FFD), and semi-permeable membranes. All three systems can be used with sensors that simultaneously measure other parameters (*e.g.*, soil conductivity, temperature). The results from these methods can be used in an ESA to develop and refine the conceptual model by identifying the contaminant location, tracing lithologic units across the site and revising geologic cross sections, tracing specific conductivity zones which may serve as preferential migration pathways, and defining the thickness and lateral continuity of aquifers, aquitards, or other definable units (*e.g.*, clay, sand lenses). The results from these *in situ* measurements can be used to effectively select sample locations and to verify the results by direct sampling and analysis with a higher DQL method.

Laser-Induced Fluorescence

Two laser-induced fluorescence (LIF) systems have been developed for use as part of a cone penetrometer test (CPT): The Rapid Optical Screening Tool (ROST™) System developed by the Air Force, and the Site Characterization and Analysis Penetrometer System (SCAPS) developed by the Navy as part of

collaborative effort with the Army and Air Force under the auspices of the Tri-Service SCAPS Program. The ROST™ system is currently available from a single CPT firm, and the SCAPS technology is available only for use by federal and state agencies.

The method uses a fiber-optic based LIF sensor deployed with a standard 20-ton cone penetrometer which simultaneously provides a continuous log of subsurface materials. Two fiber-optic cables run from the sensor up through the penetrometer rods. A pulsed nitrogen laser transmits ultraviolet (UV) light down one of the fibers to the sensor probe and through a sapphire window built into the side of the cone penetrometer tip. The UV light that exits the window causes fluorescence of the polynuclear aromatics present in the soil adjacent to the probe. The induced fluorescence signal is returned over a second fiber to the above ground analytical equipment where it is dispersed with a spectrograph and measured with a photodiode array.

The LIF system can provide qualitative information on polynuclear aromatic hydrocarbons (PAHs). The ROST™ system uses wavelength-time plots to identify the general type of petroleum hydrocarbon present. The SCAPS system is intended to provide initial information on the distribution of hydrocarbons in the soil and water prior to collecting soil cores and samples, and selecting locations for groundwater monitoring wells. It provides information on contaminant distribution with a continuous log of soil conditions.

Fuel Fluorescence Detector

A fuel fluorescence detector (FFD) has been developed for *in situ* measurement of TPH as part of a cone penetrometer test. The FFD system uses a 254-nm ultraviolet light source that is focused on soil or groundwater through a sapphire window. If aromatic hydrocarbons are present, the resulting fluorescence will return through a fiber-optic cable for analysis at the ground surface. The FFD system provides a detection limit of 100 ppm TPH (in sand), and it can detect a broad range of petroleum hydrocarbons including gasoline, diesel fuel, and jet fuel. In general, most aromatic hydrocarbons with less than four rings can be detected. Creosote cannot currently be detected with this method. Potential future developments may include the use of a spectrometer for determination of specific types of fuels.

Semipermeable Membrane Sensor

A semipermeable membrane sensor probe is an emerging technology that can be used to detect the presence of volatile hydrocarbons above and below the water table using DP rigs with percussion hammers. The sensor operates by allowing volatile constituents in the subsurface to diffuse across a thin permeable polymer membrane on the side of the probe. The inside surface of the membrane is swept with a constant flow of an inert carrier gas. Volatile hydrocarbons in the soil adjacent to the probe cross the membrane and are carried to the surface where they can be analyzed (*e.g.*, PID, FID, GC). Hydrocarbons in various phases (*e.g.*, gas, sorbed, dissolved, free product) can be detected. The lighter, more volatile constituents cross the membrane faster than heavier molecular weight hydrocarbon constituents. The membrane can operate in an ambient temperature mode or at an increased temperature of up to 250° F (121° C) to increase the movement of volatile constituents through the membrane. Heating the membrane can also significantly increase the sensitivity of the systems and decrease the time required to remove residual contaminants from the membrane.

Petroleum Hydrocarbon Analytical Equipment Manufacturers

A list of petroleum hydrocarbon analytical equipment manufacturers is included below in Exhibit VI-18. The equipment has not been evaluated by the U.S. EPA and inclusion in this manual in no way constitutes an endorsement. These vendors are listed solely for the convenience of the reader.

Exhibit VI-18
Petroleum Hydrocarbon Analytical Equipment Manufacturers

Detector Tubes	
Mine Safety Appliances Company P.O. Box 426 Pittsburgh, PA 15230 (412) 273-3000 (800) 672-2222	National Draeger, Inc. P.O. Box 120 Pittsburgh, PA 15230 (412) 788-5605 (800) 922-5518
Sensidyne, Inc. 16333 Bay Vista Drive Clearwater, FL 34620 (813) 530-3602 (800) 451-9444	
Fiber Optic Sensors	
FCI Environmental, Inc. 1181 Grier Drive Building B Las Vegas, NV 89119 (702) 361-7921 (800) 510-3627	ORS Environmental Systems 32 Mill Street Greenville, NH 03048 (603) 878-2500 (800) 228-2310
Colorimetric Test Kits	
Hanby Environmental Laboratory Procedures, Inc. 501 Sandy Point Road Wimberly, TX 78676 (512) 847-1212 (800) 304-2629	

Total Organic Vapor (TOV) Detectors (PIDs and FIDs)	
Control Instruments Corp. (FIDs) 25 Law Drive Fairfield, NJ 07004-3295 (201) 575-9114	Foxboro Analytical (FIDs and Dual FID/PID) 600 North Bedford East Bridgewater, MA 02333 (800) 321-0322
Gas Analysis Systems Company 3825 26th Street, West Bradenton, FL 34205 (914) 755-8806	HNU Systems, Inc. (PIDs) 160 Charlemont Street Newton, MA 02161 (617) 964-6690 (800) 724-5600
MSA Baseline Industries (FID/PIDs) P.O. Box 649 Lyons, CO 80450 (800) 321-4665	Photovac Monitoring Instruments (FID/PIDs) 25-B Jefryn Boulevard, West Deer Park, NY 11729 (516) 254-4199
Thermo-Environmental Instruments, Inc. (PID/FID) 8 West Forge Parkway Franklin, MA 02038 (508) 520-0430	
Turbidimetric Test Kit	
Dexsil Corporation (PetroFLAG) One Hamden Park Drive Hamden, CT 06517 (203) 288-3509	
Immunoassay Test Kits	
Strategic Diagnostics, Inc. (Includes products by D Tech, EM Science, ENSYS, Omnicon, and Millipore) 375 Pheasant Run Newtown, PA 18940 (800) 544-8881	

Portable Infrared Spectrophotometers	
Foxboro Analytical 600 North Bedford East Bridgewater, MA 02333 (800) 321-0322	General Analysis Corporation 140 Water Street, Box 528 South Norwalk, CT 06856 (203) 852-8999
Horiba Instruments, Inc. 17671 Armstrong Avenue Irvine, CA 92714 (800) 446-7422	
Portable Gas Chromatographs	
Foxboro Analytical 600 North Bedford East Bridgewater, MA 02333 (800) 321-0322	Gas Analysis Systems Company 3825 26th Street, West Bradenton, FL 34205 (914) 755-8806
HNU Systems, Inc. 160 Charlemont Street Newton, MA 02161 (617) 964-6690 (800) 724-5600	Microsensor Systems, Inc. 62 Corporate Court Bowling Green, KY 42103 (410) 939-1089
Microsensor Technology, Inc. 41762 Christy Street Fremont, CA 94358 (510) 490-0900	OI Analytical P.O. Box 9010 College Station, TX 77842 (409) 690-1711
Photovac Monitoring Instruments 25-B Jefryn Blvd., West Deer Park, NY 11729 (516) 254-4199	Sentex Sensing Technology, inc. 553 Broad Avenue Ridgefield, NJ 07657 (201) 945-3694 (800) 736-8394
Transportable Gas Chromatographs	
Gas Analysis Systems Company 3825 26th Street, West Bradenton, FL 34205 (914) 755-8806	GOW-MAC Instrument Company P.O. Box 25444 Lehigh Valley, PA 18002 (610) 954-9000
Hewlett Packard 2850 Centerville Road Wimington, DE 19808 (302) 633-8000	HNU Systems, Inc. 160 Charlemont Street Newton, MA 02161 (617) 964-6690 (800) 724-5600
Microsensor Technology, Inc. 41762 Christy Street Fremont, CA 94358 (510) 490-0900	MSA Baseline Industries P.O. Box 649 Lyons, CO 80450 (800) 321-4665

Perkin Elmer Corporation 761 Main Avenue Norwalk, CT 06859 (203) 763-1000 (888) 732-4766	Shimadzu Scientific Instruments, Inc. 7102 Riverwood Drive Columbia, MD 21046 (410) 381-1227 (800) 477-1227
SRI Instruments 3882 Del Amo Boulevard Suite 601 Torrance, CA 90503 (310) 214-5092	Varian Analytical Instruments 505 Julie River Road Suite 150 Sugarland, TX 77478 (800) 926-3000
Gas Chromatograph/Mass Spectrometer	
Bruker Instruments, Inc. 19 Fortune Drive Manning Park Bollerica, MA 01821 (508) 667-9580	INFICON Two Technology Place East Syracuse, NY 13057 (315) 434-1264
Teladyne Electronic Technologies 1274 Terrabella Mountain View, CA 94043 415 968-2211	Viking Instruments 3800 Concorde Parkway Suite 1500 Chantilly, VA 22021 (703) 968-0101
Laser Induced Fluorescence	
Fugro Geosciences, Inc. 6105 Rookin Houston, TX 77074 (713) 778-5580	
Fuel Fluorescence Detector	
Applied Research Associates, Inc. Vertek Division 120A Waterman Road South Royalton, VT 05068 (800) 639-6315	

Semipermeable Membrane Sensor	
Geoprobe Systems, Inc. 601 North Broadway Salina, KS 67401 (913) 825-1842	

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Peer Reviewers

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